Optical Measurements on Oriented Thin $YBa_2Cu_3O_{7-\delta}$ Films: Lack of Evidence for Excitonic Superconductivity

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Optical transmission and reflection spectra (mid ir through uv) and Raman spectra of superior-quality 90-, 180-, 400-, and 1000-nm-thick superconducting Y-Ba-Cu-O films are reported. Characteristic excitonic bands, and in particular the absorption band at $\simeq$0.37 eV reported earlier, are not observed. It therefore seems unlikely that the high-T_c superconductivity in cuprates could arise from exciton-mediated electron pairing.

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The discovery of high-T_c superconductivity in cuprates[1] has stimulated unprecedented research activity. Much of the effort is focused on understanding the underlying mechanism of the superconductivity, and a number of models have already been proposed.[2-4] Some of them are specific enough to be directly tested experimentally. However, what is usually the most powerful technique for identifying the mechanism, tunneling spectroscopy, has been greatly hampered so far by the generally bad surface quality of the presently available oxygen-annealed cuprate pellets and films. Infrared spectroscopy probes much deeper into the bulk of the sample and thus could play an important role in the clarification of the mechanism of superconductivity in these materials.

The optical reflectivity spectra of La-Sr-Cu-O and Y-Ba-Cu-O have been measured[5-7] over a broad frequency range (far ir through uv). However, since reflectivity depends on both the real and the imaginary parts of the dielectric function, such spectra cannot be interpreted directly in general. Orenstein *et al.*[5] tried to fit their data by the simple classical Drude model, $\epsilon(\omega)=\epsilon(\infty)-\omega_p^2/\omega(\omega+i\Gamma)$; their optimal parameter values were $\omega_p=2$ and 3 eV for La-Sr-Cu-O and Y-Ba-Cu-O, respectively, and $\Gamma=0.5$ eV and $\epsilon(\infty)=4.5$ for both compounds. The calculated reflectivity turned out to be much too large in the mid-ir and near-ir region (0.1 to 1 eV). Orenstein *et al.*[5] concluded that an optically allowed transition across a gap occurs at $\simeq$0.5 eV in La-Sr-Cu-O; a similar result was obtained for Y-Ba-Cu-O. Therefore, they inferred that the corresponding strong absorption band (with the peak absorption coefficient of $\simeq 10^5$ cm^{-1}) should be directly observable in transmission experiments on thin films. Finally, they found this ir feature to be absent in undoped La_2CuO_4, thus tying it to superconductivity. Etemad *et al.*[5] also found the correlation between the occurrence of the 0.5-eV peak and superconductivity in $La_{2-x}Sr_xCuO_4$. Kamaras *et al.*,[6] by an analogous methodology, concluded that two strong electronic transitions occur at 0.44 and 1.3 eV in La-Ba-Cu-O, and at 0.37 and 2.5 eV in Y-Ba-Cu-O. In oxygen-depleted (nonsuperconducting) $YBa_2Cu_3O_{6.2}$ samples, the 0.37-eV peak was absent. They interpreted these spectral features as the charge-transfer-exciton bands, in support of the excitonic superconductivity model of Varma *et al.*[2] Finally, Schlesinger *et al.*[7] also recorded similar spectra but derived just the opposite conclusion. Inspired by the recent report[8] of single-crystal La_2NiO_4 reflectivity spectra, which show extremely anisotropic (quasi two-dimensional) character, they concluded that no extra interband transition has to be postulated if La_2CuO_4 has similar anisotropy.

The above controversy—important in view of its implications concerning the pairing mechanism in the cuprate superconductors—can be resolved by a direct ir transmission measurement. The principal difficulty here comes from the short light penetration depth of these materials that imposes nontrivial requirements on sample preparation. Synthesis of thin Y-Ba-Cu-O films on various substrates has been reported by the Stanford University thin-film group and subsequently by several other groups.[9] Sharp (2 K wide) transitions with T_c above 90 K and high critical currents of over 2.0×10^6 A/cm^2 (at 4.2 K) have been achieved. Typical thicknesses of these films were about 1 μm; such films are not transparent in the ir region. The same is true of the usual powdered Y-Ba-Cu-O ceramics with typical particle size of 1–10 μm.

With this motivation, we have synthesized a series of 90-, 180-, 400-, and 1000-nm-thick superconducting Y-Ba-Cu-O films of various orientations, on $SrTiO_3$ substrates, using the reactive-magnetron-sputtering technique. A detailed description of the preparation and characterization method is given elsewhere.[10] X-ray diffraction shows a highly crystalline, single-phase, homogeneous, and highly oriented material. The films are optically semitransparent, uniform, and homogeneous. Resistivity measurements show extremely sharp ($\simeq 1.5$-K total onset-to-zero-resistance width) superconducting transitions at $T_c = 90$ K typically. Magnetization measurements show critical current densities in excess of 1.2×10^7 A/cm^2 at 4.2 K and 6×10^5 A/cm^2 at 78 K (for the films with the c axis oriented perpendicular to the film surface). Measurements of the angular dependence of the magnetization loops (as discussed in Ref. 10) showed a surface barrier of $\simeq 10$ kG, indicating a surface current density of 3×10^8 A/cm^2, the highest reported so far. Typical resistivity of these films in the normal state is given by $\rho \approx 1.2T + 15\ \mu\Omega$ cm, the lowest reported for these materials. The above results suggest that the films investigated were of much improved quality.

Using these films, we have recorded reflectance and transmittance spectra and Raman spectra over a broad range of frequencies and at temperatures ranging from 10 to 300 K. The infrared transmittance and reflectance measurements were made on a Biorad FTS-40 FTIR spectrophotometer coupled with a Spectratech ir microscope, and an IBM 98 (Bruker) FTIR interferrometer. For the Raman scattering experiment an Ar^+-ion laser, a Spex triple-scanning monochromator, and a cooled GaAs photomultiplier detector were utilized. The same monochromator and detector, as well as a Varian-Cary double-beam spectrophotometer, were utilized to record the near-ir through uv transmittance spectra.

The first observation is that our films show much higher mid-ir specular reflectance than the ceramic samples of Refs. 5 and 6, and, in fact, higher than the Drude-model fit of Orenstein *et al.*[5] In Fig. 1 we show our reflectance data of a polycrystalline film together with the data of Refs. 5 and 6. No extra absorption peak at $\simeq 0.4$ eV is inferred from the data. This reflectance spectrum can well be fitted by a simple Drude model, with $\omega_p = 2.6$ eV, $\Gamma = 0.65$ eV, and $\epsilon(\infty) = 4.5$.

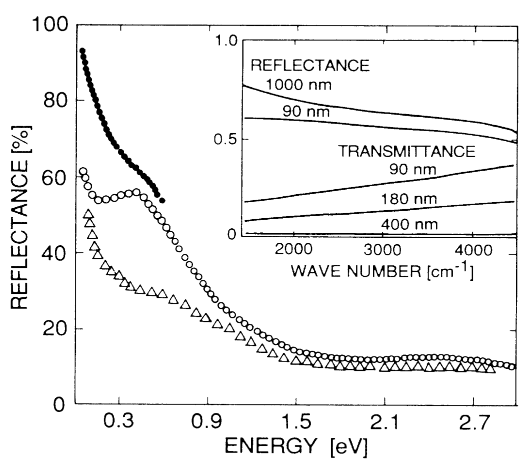

FIG. 1. Reflectance from randomly oriented 1-μm-thick film (filled circles), compared to bulk-ceramic Y-Ba-Cu-O data of Orenstein *et al.* (Ref. 5) (open circles) and Kamaras *et al.* (Ref. 6) (triangles). Inset: Mid-ir reflectance (upper two curves) and transmittance (lower three curves) of films with various thicknesses.

An independent and direct proof of this conclusion comes from the transmittance spectra of the films which are featureless in this frequency range (see inset of Fig. 1). All other samples of comparable quality—over a dozen films, of various orientations—showed similar spectra. Note the transmittance and reflectance of the 90-nm film which indicate a substantial absorption background.

The Raman spectra of these films also show an electronic background which is featureless (see Fig. 2). Finally, no peaks emerged in either the ir or the Raman spectra at lower temperatures, down to 10 K (scanning densely the region around T_c).

The absence of exitonic resonances in our ir and Raman spectra still leaves a remote possibility that an excitonic transition exists, but it is neither dipole nor quadrupole allowed. In more detail, the space group of $YBa_2Cu_3O_7$ is D_{2h} (*Pmmm*), and the maximal site symmetry [enjoyed by Cu(1) and O(1) atoms] is D_{2h}^1. This group does have one "silent" (i.e., optically inactive) irreducible representation, A_u—the one that is odd with respect to each of the three symmetry planes *ab*, *ac*, and *bc*. However, to within a few electronvolts above E_F, in $YBa_2Cu_3O_7$ there are no transitions that reverse the parity with respect to each of these three mirror planes. Moreover, to be relevant for superconductivity, the excitons have to be mobile, but any dispersion would make direct ($\Delta k = 0$) transitions into all but a few (Brillouin-zone center and edge) excitonic states ir and/or Raman allowed.

Therefore, it seems that in $YBa_2Cu_3O_7$ there are no excitons close to the Fermi level, such as have been assumed to be necessary[3] for excitonic superconductivity. In fact, we have recorded the transmittance spectra of

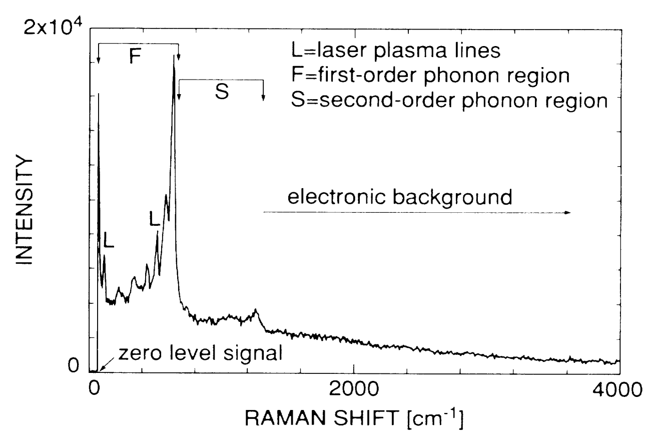

FIG. 2. Raman scattering (at 300 K) from a good superconducting film (400 nm thick, *a*-axis oriented).

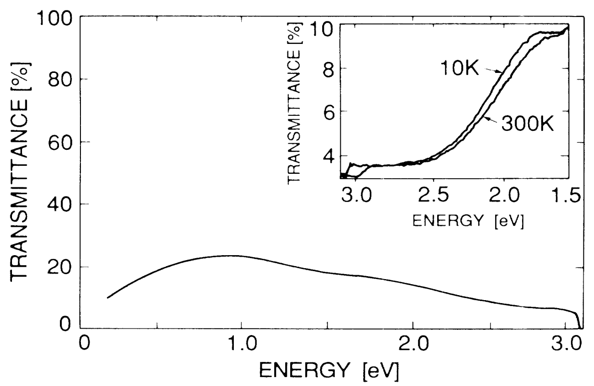

FIG. 3. ir to uv transmittance spectrum of 180-nm, c-axis-oriented film. Inset: Interband transition edge on an expanded scale.

$YBa_2Cu_3O_7$ films from mid ir through uv (0.1 to 3.5 eV), and observed no sharp absorption peaks expected for excitonic states (Fig. 3). Hence, we believe that excitons—at least in the usual sense of Frenkel excitons, charge-transfer excitons,[2] or Wannier-Mott excitons—are not formed in our superconducting $YBa_2Cu_3O_7$ samples. This should not be surprising, in view of their high conductivity, approaching that of Bi or Hg.

It may be relevant to note that some of the films prepared earlier, which had somewhat inferior superconducting characteristics (broader transitions, smaller critical current densities, less homogeneity) did show a broad absorption feature in the ir measurements centered at about 2500–3000 cm^{-1} (0.3–0.4 eV) with a similar feature in the Raman spectrum. However, this feature is not nearly as pronounced as was concluded in Refs. 5 and 6. This band is very broad, in contrast to usually rather narrow excitonic features. Both the strong Raman peak and the weak ir feature are seen at room temperature and show little temperature dependence. Thus it seems that this electronic transition is not characteristic of the high-T_c superconducting material, but rather of some structurally or compositionally disordered regions in less homogeneous samples. The important point that we stress here is that good superconducting films exist without any trace of the 3000 cm^{-1} ir band.

In conclusion, we have prepared superconducting Y-Ba-Cu-O films thin enough to enable high-quality mid-ir through uv absorption measurements. In contrast to some earlier reflectivity studies,[5,6] no spectroscopic features suggestive of excitonic absorption are seen. It thus seems unlikely that observed high-T_c superconductivity in Y-Ba-Cu-O originates from exciton-mediated electron pairing. Moreover, no other sharp bosonic excitations (e.g., magnons) are detected either. The strong but featureless absorption we observed is more suggestive of fermions (e.g., polarons)—perhaps quasilocalized in view of the temperature-independent interband-transition-edge smearing, the large damping, and the low Hall mobility ($\simeq 8$ cm^2/V-s for good c-axis films) that we have measured on these films.

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[1]J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986); M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987).

[2]C. Varma *et al.*, Solid State Commun. **62**, 681 (1987).

[3]W. A. Little, in *Proceedings of the International Workshop on Novel Mechanisms of Superconductivity, Berkeley, California, 1987,* edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987); J. Bardeen *et al.*, *ibid.*; J. Yu *et al.*, *ibid.*

[4]P. W. Anderson, Science **235**, 1196 (1987); S. Kivelson *et al.*, Phys. Rev. B **35**, 8865 (1987); D. Pines, in Ref. 3; S. Doniach, in Ref. 3; V. Kresin, Phys. Rev. B **35**, 8716 (1987); J. Ruvalds, Phys. Rev. B **35**, 8869 (1987); V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987); P. G. de Gennes, to be published.

[5]J. Orenstein *et al.*, Phys. Rev. B **36**, 729 (1987); S. Etemad *et al.*, to be published.

[6]K. Kamaras *et al.*, Phys. Rev. Lett. **59**, 919 (1987); S. L. Herr *et al.*, Phys. Rev. B **36**, 733 (1987).

[7]Z. Schlesinger *et al.*, in Ref. 3.

[8]J. M. Bassat *et al.*, Phys. Rev. B **35**, 7126 (1987).

[9]A. Kapitulnik *et al.*, Int. J. Mod. Phys. B **1**, to be published.

[10]K. Char *et al.*, Appl. Phys. Lett. (to be published); B. Oh *et al.*, Appl. Phys. Lett. **51**, 852 (1987).